

FINAL REPORT

ION IMPLANTED EPITAXIALLY GROWN ZnSe

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ABSTRACT

The epitaxial growth of ZnSe on (100) Ge using the close-spaced transport process is described. Substrate temperature of 575°C and source temperatures of 675°C yield 10 micron, single crystal layers in 10 hours. The Ge substrate provides a nonreplenishable chemical transport agent and the epitaxial layer thickness is limited to approximately 10 microns. As grown epitaxial layers show excellent photoluminescence structure at 77°K. As grown layers exhibit high resistivity, annealing in Zn vapor at 575°C reduces the resistivity to 10-100Ω-cm. Zinc vapor annealing quenches the visible photoluminescence.

INTRODUCTION

The literature on the epitaxy of ZnSe on Ge is relatively large. Growth techniques include vacuum deposition,^{1,2,3} chemical vapor transport,⁴ close-space, vapor transport,⁵ and close-space, chemical vapor transport.⁵ The pair of semiconductors is particularly attractive for electronic applications such as transistors with wide band gap emitters^{6,7} due to the small lattice mismatch and low concentration of interface states achievable.⁸ Vacuum deposited layers exhibit strain and adhesion problems that may make them unacceptable for devices.^{1,2} Chemical transport techniques lead to incorporation of substantial halogen concentrations which create donors and comparable densities of deep acceptors.^{4,5,9} The close-spaced growth process using pure H₂ gas and undoped ZnSe sources minimizes doping and compensation in a configuration that is inherently clean and efficient.¹⁰

The present work was motivated by a need to prepare ZnSe substrates suitable for ion implanted, electroluminescent devices. Required characteristics include morphology adequate for ion implantation, low doping to minimize the dose required for compensation, and high luminescence efficiency. Layers grown using the close-space technique were examined for morphology and macroscopic uniformity, behavior under Zn vapor annealing, and photoluminescence structure. Photoluminescence measurements provide information on both the defect structure of the ZnSe layer and a suggestion of its electroluminescence potential. Little has been reported on the photoluminescence of ZnSe epitaxial layers and the reported results are somewhat disappointing.⁴

ANALYSIS TECHNIQUES

Surface morphology was observed using a 27X to 1250X microscope with a Nomarski phase contrast attachment. The front surface of the ZnSe layer was always examined; in some cases the ZnSe layer was removed by etching in 5% Bromine in methanol to permit examination of the Ge substrate for etching by Se vapor during growth.⁵ Samples were cleaved for microscopic examination to determine the thickness of the ZnSe layers. Uniformity of both the growth and substrate etching were also noted. Crystallinity of the ZnSe layers was examined using Laue X-ray reflection and glancing, high energy electron diffraction techniques. As a consequence of the thin layers ($\leq 10\mu$) and good lattice match, the X-ray data is dominated by reflections from the substrate.

Several samples were annealed in a Zn vapor atmosphere at 575°C. No attempt was made to protect the Ge substrate from attack by the Zn vapor, and this precluded annealing in liquid Zn.⁵ The samples were placed in high purity quartz ampoules with a weighed quantity of metallic Zn (99.9995 pure) sufficient to achieve the Zn_l - Zn_g equilibrium at the annealing temperatures while minimizing the quantity of excess, liquid Zn.^{11,12} The ampoules were evacuated to 10^{-6} Torr and sealed. Annealing was performed for times between 1 hr and 36 hrs. The ampoules were inserted into a preheated furnace and quench-cooled upon removal.

Annealed samples were examined for cracks and peeling which would indicate stress and adhesion problems. Four terminal resistivity measurements were performed, and the ZnSe layer was etched

back in steps and the resistivity measurement repeated to determine the uniformity of the induced conductivity.

UV stimulated luminescence measurements were performed to assess the quality of the ZnSe epitaxial layers. Samples were clamped to a cold finger in an evacuated Dewar and held at liquid nitrogen temperature. Light from a high pressure, 100W mercury lamp was filtered (Corning #7-51) to remove visible components and focused on the sample. The spectrum was resolved using a double pass monochromator and detected using a photomultiplier with an S-10 photocathode. None of the spectra were corrected for system response.

GROWTH SYSTEM

The close-space transport system employed in this work is shown in Fig. 1. This configuration is similar to that described by Hovel and Milnes.⁵ The insert in Fig. 1 shows the actual growth region. The high purity quartz crown establishes the source to substrate separation and aids in controlling the vapor pressure over the substrate. Slots cut in this crown provide access for the flow gas. Several variations in the access area were used, but no dependence of the growth behavior on this area could be determined. The source and substrate are clamped by high purity, low porosity carbon blocks which act as absorbers heated by external 600W tungsten-iodide lamps. These susceptors are supported by high purity quartz tubes. Thermocouples inserted in these tubes are used to monitor

the temperatures of the susceptors and control the power to the lamps. Dual digital set point indicators, current modulators, and SCR power circuits control the substrate temperature (T_{sub}) and the source-substrate temperature difference (ΔT). Rapid response with little or no overshoot and temperature control of better than 1°C was easily achieved.

A gas flow and mixing system was designed to accommodate HCl chemical transport growth as well as the work described here. It was constructed of monel, type 316 stainless steel, and inert plastics. This system was made leak tight to within the 10^{-10} atm-cc/sec sensitivity of a helium leak detector. The hydrogen flow gas used during the growths was palladium-diffusion purified. Electronic grade HCl and prepurified argon were employed. Argon was used as a continuous flushing gas when the systems were not in use. (This involved flushing several glass envelope-susceptor systems that were used exclusively for substrate and flow gas combinations other than Ge and H_2 .) Systems were open to the atmosphere for source or substrate replacement for a few minutes at most. Prior to growth, the growth region was baked at 350°C in flowing H_2 for a minimum of one hour.

Substrate and Source Preparation

Substrates were prepared from 2/3 mm thick, (100) oriented Germanium wafers. The Ge was nominally undoped (40-100 $\Omega\text{-cm}$, p-type). Normal dependence of epitaxial layer morphology on

substrate surface structure was complicated by selective Se etching of the Ge during growth. The best results in terms of ZnSe uniformity and surface morphology were obtained when the substrates were mechanically polished using 1μ Al_2O_3 and then etch polished using concentrated NaOCl on a low nap pad.¹³ This produces optically flat, scratch-free Ge surfaces. A final etch in dilute I_2 - HF to remove 3-5 mils was used to reduce surface damage resulting from the polishing procedure.

Since the close-space transport is very efficient, approximately twenty 10 micron thick growths can be made before the source-substrate gap changes appreciably. The work described here is the result of two separate source charges of which each were used twenty times. Sources were prepared from two separate high purity ZnSe single crystals. Both crystals had high dark resistivity and both contained numerous grain boundaries. Emission spectroscopy revealed an impurity concentration of 540 ppm (500 ppm Si, 20 ppm Fe) in the first crystal and an impurity concentration of 70 ppm (50ppm Si, 20 ppm Fe) in the second crystal. These emission spectroscopy estimates exclude copper which was measured by atomic absorption at 87 ppm and 0.4 ppm, respectively. The first crystal was ground down to $\sim 50\mu$ grains to form a "crushed crystal" source. The second crystal was cut and polished to fit the quartz crown to form a "single crystal" source. Surface damage and contamination was removed by etching in H_2SO_4 - $\text{K}_2\text{Cr}_2\text{O}_7$ in the latter case.¹⁴

GROWTH

T_{sub} and ΔT were varied from 550°C to 800°C and 5°C to 125°C, respectively, to determine optimum growth conditions. Optimum conditions for this case are defined as best surface morphology, best crystal structure, with acceptable growth rate. The optimum conditions were $T_{\text{sub}}=575^\circ\text{C}$, $\Delta T=100^\circ\text{C}$ at a hydrogen flow of 300 cc/min.

Ten micron thick films were grown in 10 hours under optimum conditions. Increasing T_{sub} leads to severe pitting of the Ge substrate while almost no pitting was observed under optimum conditions. There is always evidence of Ge etching in the area where the quartz crown makes contact with substrate. At the inside diameter of the crown, erosion reaches depths of a few microns. This erosion decreases continuously toward the outside diameter where isolated, square etch pits are found. No etching is observed outside the crown except in the immediate neighborhood of the slots. decreasing ΔT increases substrate pitting as well as reducing the growth rate. For $T_{\text{sub}}=575^\circ\text{C}$, ΔT must be greater than 50°C for the ZnSe thickness to exceed the erosion depth of the substrate. As T_{sub} is increased, ΔT must also be increased for this condition to be met. Increasing ΔT above 125°C leads to faceting and macroscopic nonuniformity of the layer but HEED and X-ray analysis indicated that all the epitaxially grown films were single crystal.* T_{sub} must exceed 500°C to achieve usable growth rates.

*Experiments were performed to determine the growth rate for the single crystal to polycrystal transition at the optimum substrate temperature. Addition of 0.6% HCl leads to a growth rate of 30 μ /hr and induces this transition. This agrees with a linear extrapolation of the transition data for ZnSe epitaxy on (100) Ge presented by Calow et al.²

It has not been possible to define a ZnSe growth rate for this configuration. Increasing the growth time from 10 to 20 hours does not increase the layer thickness by more than 20%. Similar evidence for saturation of the layer thickness is found when the growth time is reduced. Any conclusions, however, must be qualified due to a $\pm 20\%$ uncertainty in the layer thickness under supposedly identical conditions.

The first series of growths were performed using the crushed crystal source. A Nomarski photograph of the ZnSe layer produced in Run #12 is shown in Fig. 2a. The source had been used for 54 hours growing time prior to this run without replenishment. Earlier runs show projecting yellow needles as well as the uniform epitaxial layer. The density of dendritic needles decreases continuously to zero over the first 75 hours of source use. There also appears to be some improvement in the uniformity of the continuous layer with each succeeding growth.

Figure 2b is a Nomarski photograph of a ZnSe layer produced using the single crystal source after 144 hours of prior use. In contrast to the powder source results, dendritic growth appears in only the first epitaxial layer and no further systematic changes occur in the morphology of the epitaxial layers.

PHOTOLUMINESCENCE

Figure 3 shows the visible photoluminescence spectra of a series of ZnSe layers grown using the crushed crystal source. The chronological sequence of the growths is indicated by the run

number; all of these growths were performed with approximately optimal parameter values. There is also a reduction in dendritic growth in this progression. The dendritic growth was brushed off the sample prior to taking the spectra shown in Fig. 3. Etching to remove any residue of the dendrites did not alter the spectra.

The evolution of the luminescence from layer to layer using the same source is too complex to be described completely by Fig. 3. The epitaxial layers grown when the source is new are of relatively poor quality and the luminescence is characterized by a broad, weak line peaking between 5900\AA and 6100\AA . As the source is used, epitaxial layers exhibit a 5400\AA line of increasing intensity followed by the gradual appearance of a line at 6240\AA and simultaneous decrease in the intensity of the 6000\AA line (#7). In turn, the 6240\AA line decays and what appears to be an unresolved pair of lines at $\sim 6000\text{\AA}$ and $\sim 5600\text{\AA}$ grows in intensity. Still later growths from the same source result in epitaxial layers that exhibit a reduction in intensity of the 6000\AA line with no change in the 5625\AA line. Appearance of the blue emission band at $4560\text{-}4720\text{\AA}$ and the line at 4450\AA occurs with extinction of the 6000\AA band (#10). Continued use of the source leads to epitaxial layers that show increased intensity and better resolution in the blue emission band (#13).

Run #17 was performed on a GaAs substrate. A 5μ epitaxial ZnSe layer was grown on the (100) GaAs substrate in ten hours. T_{sub} and ΔT were maintained at 575°C and 100°C , respectively. In contrast to normal procedure, neither the growth tube nor the ZnSe source were changed. Figure 3 #17 shows substantial intensity

enhancement and line width reduction of the 5625\AA line. No other lines were observed in the spectra. Run #17 was followed by additional growths on germanium substrates using the same source and growth tube. Figure 3 #18 shows the luminescence spectra of an epitaxial layer contaminated with Ga and As. The 6240\AA red band reappears and the blue band loses its structure and is shifted to longer wavelength. Figure 3 #19 (a spectrum of the next epitaxial layer grown in the same apparatus but with the source of contamination removed) indicates a return to the spectrum shown in Figure 3 #13 and purification of the apparatus. Later runs show that the return to the original spectra is erratic and slower than might appear from the data appearing in Fig. 3 #18 and #19.

Figure 4 details the behavior of the blue emission band. The phonon assisted emission series seen in the run #13 sample has been identified as resulting from a free to bound transition by Dean and Merz.¹⁵ The LO phonon energy implied is $30.5 \pm 1 \text{meV}$ in agreement with published results.^{15,16} Application of Hopfield's theoretical formula for the peak amplitudes yields a mean phonon coupling \bar{N} of 0.5 to 0.6. This result appears to be typical for ZnSe.^{15,16} The blue emission band for the run #18 sample is typical of ZnSe with high Al and Na concentrations.¹⁶ The line at 4450\AA is a combination of unresolved I_1 , I_2 , and I_x lines.¹⁷

ZnSe layers grown from single crystal sources show similar luminescence spectra with notable exceptions. The structure of the blue emission changes in an erratic manner from growth to growth and never develops the detail observed in the spectra of the epitaxial layers grown from the powdered source. The 4450\AA

line is observed in all epitaxial layers from the onset of use of the source. Layers grown during the initial runs show the 5600Å band whereas the 4560-4720Å band is absent. The broad 6000Å emission band may appear alone or with a line at approximately 5400Å. Other epitaxial layers exhibit a 6240Å emission band appearing with a line peaking anywhere between 5600Å and 5440Å. The 4560-4720Å blue emission band is present only when the 6000Å band is absent. Luminescence intensity in epitaxial layers grown from both sources is comparable.

Although growth of ZnSe epitaxial layers using HCl as a chemical transport agent is not the subject of this paper, some reference to the luminescent spectra obtained is useful. Layers grown using single crystal sources and less than 0.1% HCl in H₂ show a green emission band centered at 5250Å. At higher HCl concentrations the layers show a broad 6000Å band and the blue emission is either structureless and very weak or absent. The photoluminescence spectra indicates no persistent contamination of the ZnSe source as a result of using HCl. Cutting off the HCl flow yields epitaxial layers showing 6240Å and 5400Å emission bands and good blue emission in the following growth.

Sources used in HCl also show ~6200Å and ~5400Å emission bands but do not show either intense or highly structured blue emission. Examination in regions with and without exposed grain boundaries shows that most of the emission originates at the grain boundaries. Small shifts in the peak wavelengths and changes of the line width of both the ~6200Å and 5400Å band demonstrate that the higher intensity observed at grain boundaries

is not due to scattering. Unused source wafers do not exhibit uniform luminescence intensity or structure except that blue emission is usually not present. Sources used in H_2 only show a single weak luminescence band peaking at $5400\overset{\circ}{\text{A}}$.

ZINC ANNEALING

All as-grown epitaxial layers exhibit resistivities greater than $10^8 \Omega\text{-cm}$ as measured with a four-point probe. Uncertain junction isolation between the n type epitaxial layer and the p type substrate sets this value as a lower limit. Annealing in saturated Zn vapor at 575°C for 18 hours reduces the resistivity to $10\text{-}100\Omega\text{-cm}$. Etching studies indicate that the conductivity modification is uniform throughout the epitaxial layer thickness. Similar changes are observed upon annealing ZnSe source crystals under the same conditions. These results are typical of bulk ZnSe.¹⁵ In contrast to bulk ZnSe crystals annealed under these conditions, ZnSe epitaxial layers grown on Ge by H_2 transport show no visible photoluminescence at 77°K . Etching experiments demonstrate that this absence persists throughout the layer. Annealing in saturated Zn vapor at 575°C for times such that the resistivity is reduced to the $10^4 \Omega\text{-cm}$ range results in a four-fold reduction in luminescence intensity and broadening of the blue emission lines.

It might be hypothesized that photoluminescence is killed by a deep trapping and recombination center. Hovel has reported a

Ge-ZnSe heterojunction switching device that depends on the presence of deep traps.¹⁸ Measurements on these annealed samples do not show switching behavior strongly suggesting that deep traps are not present.

Annealed samples did not exhibit lifting or cracking. In contrast to other ZnSe-Ge epitaxy studies employing different deposition techniques and/or thickness, this work did not show an adhesion or stress problem that can be revealed by annealing.

DISCUSSION

Approximately 10 micron thick ZnSe layers can be grown on (100) Ge using the close space technique without using a chemical transport agent. Nonlinearity in the growth rate confirms Hovel and Milnes' observation that Ge itself acts as a chemical transport agent.⁵ Hovel and Milnes also obtained no growth on GaAs (B surface) under conditions similar to those used here; i.e. $T_{\text{sub}}=590^{\circ}\text{C}$, $\Delta T=110^{\circ}\text{C}$, and 0.02% HCl in H_2 . (HCl should increase the growth rate but we have not observed measurable increases at this low concentration.) In contrast, a 5 micron thick ZnSe layer was obtained ($T_{\text{sub}}=575^{\circ}\text{C}$, $\Delta T=100^{\circ}\text{C}$, and pure H_2) on (100) GaAs using a source that had been used for repeated growths on Ge. Although conditions are not identical, the most probable explanation for the discrepancy is persistent Ge contamination of the source powder. Parker et al. obtain Ge concentrations of 50-100 ppm in ZnSe epitaxial layers grown by HBr transport on $\sim 500^{\circ}\text{C}$ Ge substrates,⁴ and Hovel

and Milnes demonstrate that this Ge is provided by Se rather than halogen etching of the substrate.⁵ It must be concluded that under optimum growth conditions when there is no visible etching under the ZnSe layer the GeSe_x concentration is replenished via etching at the quartz crown-substrate interface. Etching in only this region implies very low Zn and ZnSe mobility on the substrate surface and very fast reaction of H_2Se with the exposed Ge. Slightly higher substrate temperature at this interface may also enhance the selectivity of the etching.

Gradual changes in the morphology of layers grown from the crushed crystal source and absence of similar changes in layers grown from the single crystal source can be explained by several models. The large surface area of the crushed crystal source, uncertain thermal contact, and latent heat of vaporization may cooperate to yield supersaturation and dendritic and atypical growth. Morphology improves as smaller grains are consumed or "fused" together to reduce the surface area and improve thermal contact. It is also possible that the ZnSe source surface must equilibrate at nonstoichiometric Zn and Se concentrations in order to achieve stoichiometric deposition. The higher impurity concentration of the crushed crystal source may have an adverse effect on morphology. Crushing ZnSe also exposes grain boundary surfaces and the impurity concentration on these surfaces is expected to be higher than the bulk. Repeated sublimation from these surfaces may lead to successively purer epitaxial layers.

The photoluminescent spectra of the best epitaxial layers is superior to both that previously reported for epitaxial layers^{9,19}

and the source crystals employed in this work. "Superior" in this case refers to the dominance and structural detail achieved in the blue emission region. Blue emission has been identified with Na acceptors,¹⁶ but the origin of Na has not been established. Emission spectroscopy reveals no Na in the ZnSe sources and 2 ppm Na in the graphite absorbers. The Ge substrates were not analyzed.

The consistent reduction of the long wavelength emission of layers grown from the crushed crystal source and the erratic behavior of this emission in layers grown from the single crystal source suggests that with the exception of the 5625Å line these lines are associated with chemical impurities originating preferentially from grain boundaries in the source. An abnormally high concentration of chemical impurities at grain boundaries is expected and examination of the source luminescence confirms a higher concentration of optically active defects at grain boundaries. Crushing the source exposes these high impurity concentration regions so they are sublimed and incorporated in the early grown epitaxial layers. Single crystal sources release these impurities for incorporation as sublimation and preferential sublimation at grain boundaries exposes impurity pockets. This model requires that these impurities do not both diffuse freely along the grain boundaries and sublime preferentially at the source surface.

Only speculative identifications can be made as to the specific origin of the long wavelength lines. The luminescence band at 6000Å is thought to be equivalent to the self-activated blue luminescence center in ZnS.²⁰ This center has been suggested to consist of a Zn vacancy associated with a halogen or a group III donor.²¹ Appearance of this line in layers grown in high HCl concentrations

suggests the halogen donor is responsible. Failure to observe the 6000\AA line and the blue emission series simultaneously suggests that the halogen concentration is normally small compared to the Na concentration in epitaxial ZnSe layers grown by H_2 transport.

Cu has been associated with emission bands at approximately 5300\AA and 6300\AA .^{19,21,23,24} Aven and Halstead observed green emission in compensated ZnSe:Cu:Cl and red emission in ZnSe:Cu:Al in regions containing excess Cu.²¹ Cl does not appear to be optically active in the former case while an optically active Cu-Al complex appears to form in the latter case.^{21,25} Similar processes may lead to the 5250\AA band in layers grown using low HCl concentration and reappearance of the 6240\AA band after contamination of the growth apparatus with Ga.¹⁹ The relative behavior of layers grown from the two sources is not consistent with the initial Cu concentrations however. For example, the 6240\AA emission may be a self-activated band associated with group III donors.^{7,25}

Both the 5625\AA line in layers grown from the crushed crystal and the 5600\AA - 5440\AA line in layers grown from the single crystal appear to be the so-called yellow self-activated luminescence.²⁶ Variability in the peak in the latter case is thought to be due to a varying defect concentration. The narrower 5625\AA line resulting from Ga and As contamination probably arises from a different type of center.

The ZnSe source material used for this study is similar to that employed by Dean and Merz and by Chatterjee et al. in regard to both electrical and photoluminescent behavior.^{15,16} Prior to Zn vapor annealing the epitaxial layers also exhibited similar photoluminescent

behavior. The initial conductivity of the epitaxial layers and their response to Zn vapor annealing is also similar. Dean and Merz annealed their ZnSe samples in Zn vapor to create or enhance the Q and Q^{F→B} emission lines.¹⁵ This procedure should reduce the Zn vacancy concentration. Chatterjee et al. indicate that Na substituting for Zn is responsible for the Q emission series.¹⁶ The presence of substitutional Na must be accompanied with a reduction in Zn vacancies if the blue emission is to be enhanced. If not, the deeper Zn vacancies would tend to dominate the photoluminescence and lead to longer wavelength emission. The epitaxial layers show no visible photoluminescence when Zn vapor annealed to achieve similar electrical properties. This implies either that a killer center involving Ge impurities is formed or that the optically active centers are gettered by the substrate.

Approximately 75 hours of firing the source powder at the growth temperature is an impractical method for stabilizing and purifying the source material. Even this preparation does not achieve surface morphology comparable to that obtained using a single crystal source. It is possible that prefiring single crystal sources in liquid zinc would make these sources more uniform and achieve some purification by a solvent extraction process.²⁷

REFERENCES

1. Calow, J.T., S.J.T. Owen and P.W. Webb, Phys. Stat. Sol. 28, 295 (1968).
2. Calow, J.T., D.L. Kirk and S.J.T. Owen, Thin Solid Films 9, 409 (1972).
3. San, A., J. Appl. Phys. 44, 523 (1973).
4. Parker, S.G., J.E. Pinnell and L.N. Swink, J. Phys. Chem. Solids 32, 139 (1971).
5. Hovel, H.J. and A.G. Milnes, J. of Electrochemical Soc. 116, 843 (1969).
6. Kroemer, H., Proc. IRE 45, 1535 (1957).
7. Hovel, H.J. and A.G. Milnes, IEEE Trans. ED-16, 766 (1969).
8. Milnes, A.G. and D.L. Feucht, Heterojunctions and Metal-Semiconductor Junctions, New York, Acad. Press (1972).
9. Parker, S.G., J. of Crystal Growth 9, 177 (1971).
10. Nicoll, F.H., J. of Electrochemical Soc. 110, 1165 (1963).
11. Honig, R.E., RCA Rev. 23, 567 (1962).
12. Goldfinger, P. and M. Jeunchemme, Trans. Faraday Soc. 59, 2851 (1963).
13. Reisman, A. and R. Rohr, J. of Electrochemical Soc. 111, 1425 (1964).
14. Park, V.S., C.R. Geesner and B.K. Shin, Appl. Phys. Lett. 21, 567 (1972).
15. Dean, P.J. and J.L. Merz, Phys. Rev. 178, 1310 (1969).
16. Chatterjee, P.K., A.J. Rosa and B.G. Streetman, J. of Luminescence 8, 176 (1973).
17. Rosa, A., private communication.
18. Hovel, H.J., Appl. Phys. Lett. 17, 141 (1970).
19. Roindessault, C. Auzary and F. Lebourg, C. R. Acad. Sci. Paris 272, 691 (1971).
20. Prener, J.S. and D.J. Weil, J. Electrochem. Soc. 106, 409 (1959).

21. Aven, M. and R. Halstead, Phys. Rev. 137A, 228 (1965).
22. Iida, S., J. of Phys. Soc. of Japan 25, 177 (1968).
23. Stringfellow, G.B. and R.H. Bube, Phys. Rev. 171, 903 (1968).
24. Markovskii, L. Yz., I.A. Mironov and Yu. S. Ryzhkin, Bull. Acad. Sci. USSR 33, 887 (1969).
25. Parker, S.G. and J.E. Pinnell, Trans. Metallurgical Soc. of AIME 245, 451 (1969).
26. Iida, S., J. of Phys. Soc. Japan 26, 1140 (1969).
27. Aven, M. and H.H. Woodbury, Appl. Phys. Lett. 1, 53 (1962).

Figure #1

ZnSe growth system

Graphite absorbers are 1 1/2" DIA x 7/16" thick; Ge substrates are 1/2" square, and the ZnSe growth region is 0.34" in diameter. Gases are vented through bubblers to prevent back diffusion. For H₂+HCl growths pure H₂ flows through the Ar flow gauge and a large fraction of the initial H₂+HCl mixture is dumped at the purge port in order to obtain low HCl concentrations.

Figure #2a

Surface of ZnSe epitaxial layer grown from the crushed crystal source: Nomarski phase contrast; calibration marks correspond to 5 microns.

Figure #2b

Surface of ZnSe epitaxial layers grown from the single crystal source: Nomarski phase contrast; calibration marks correspond to 5 microns.

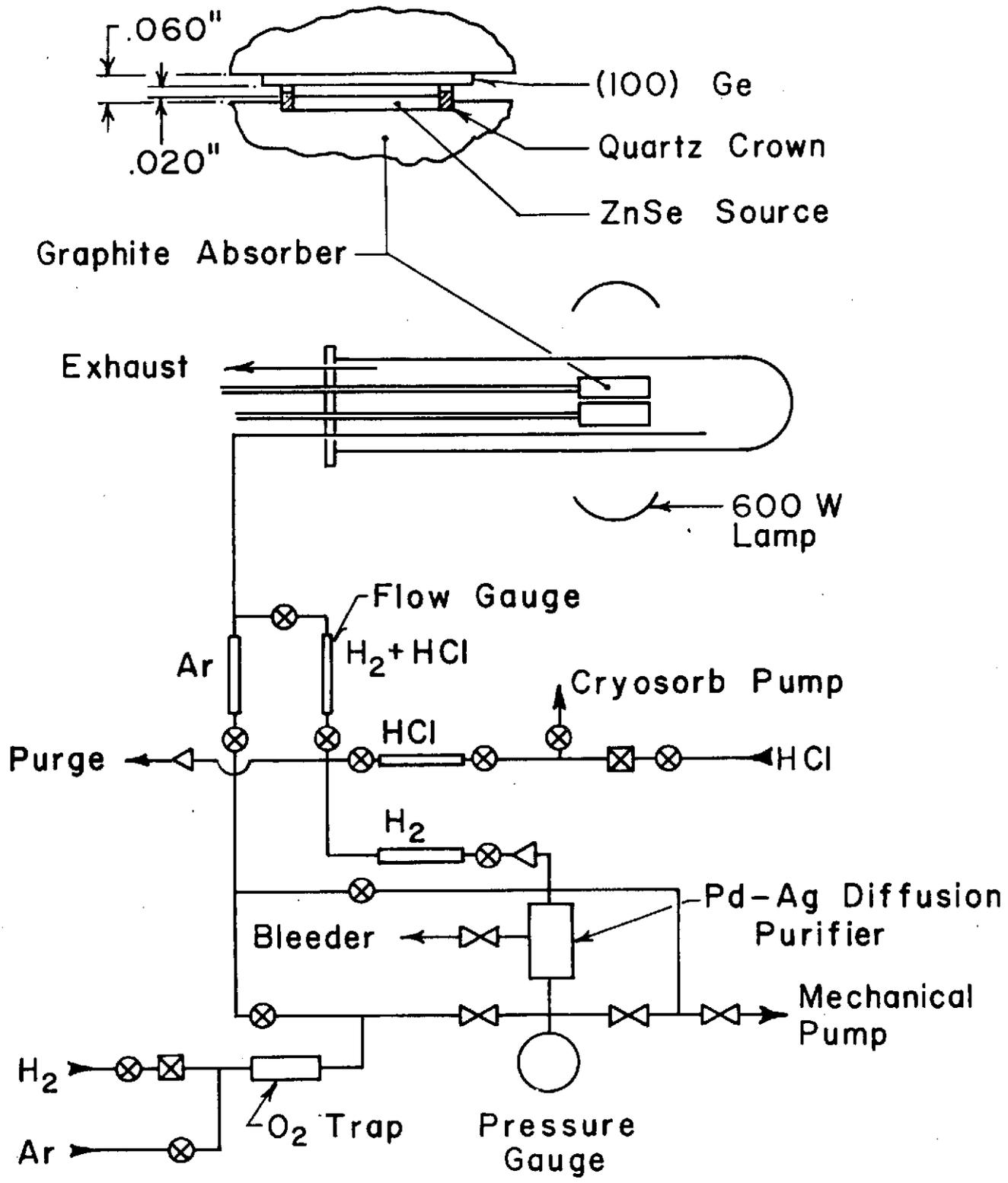


Figure 1

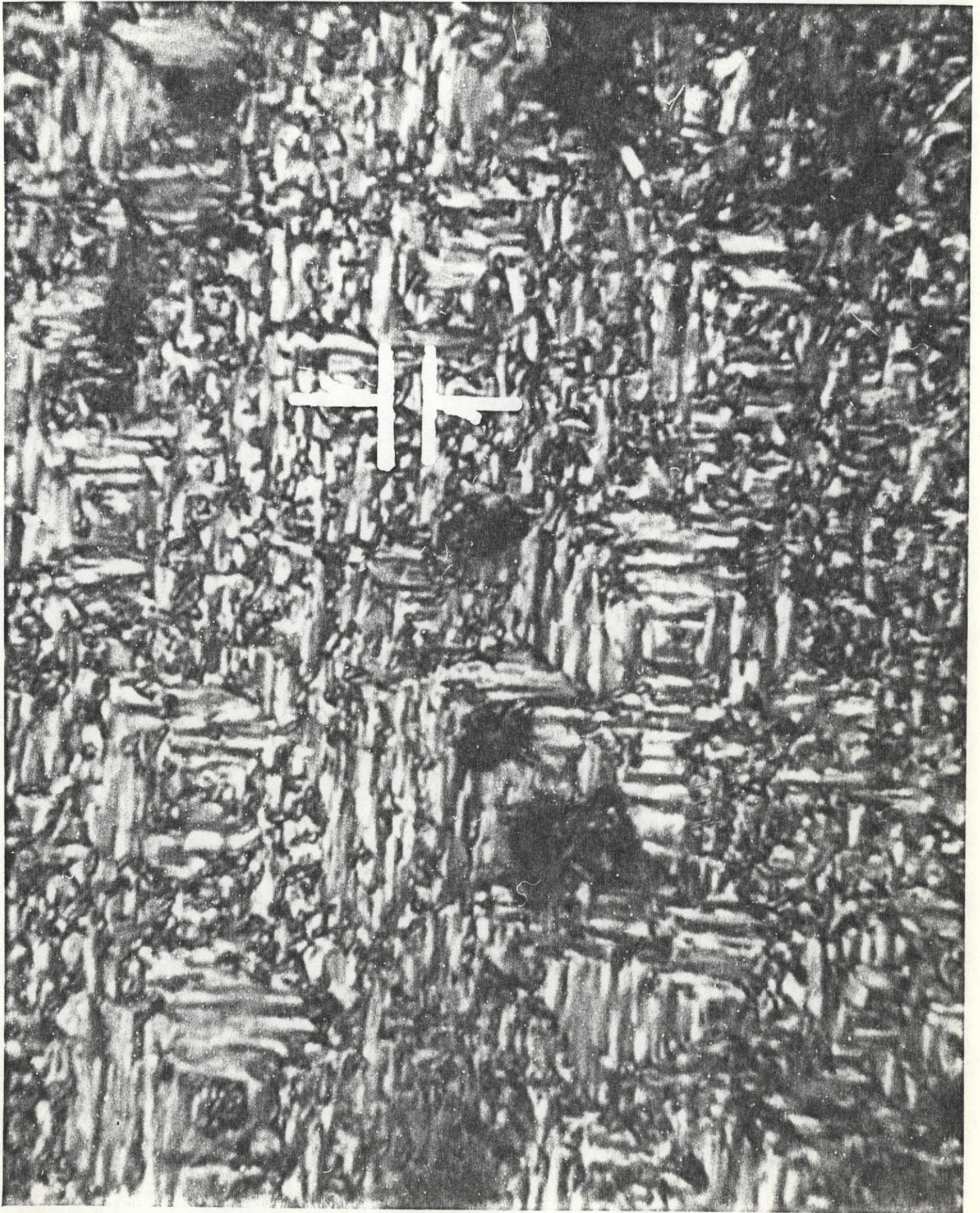


Figure 2a

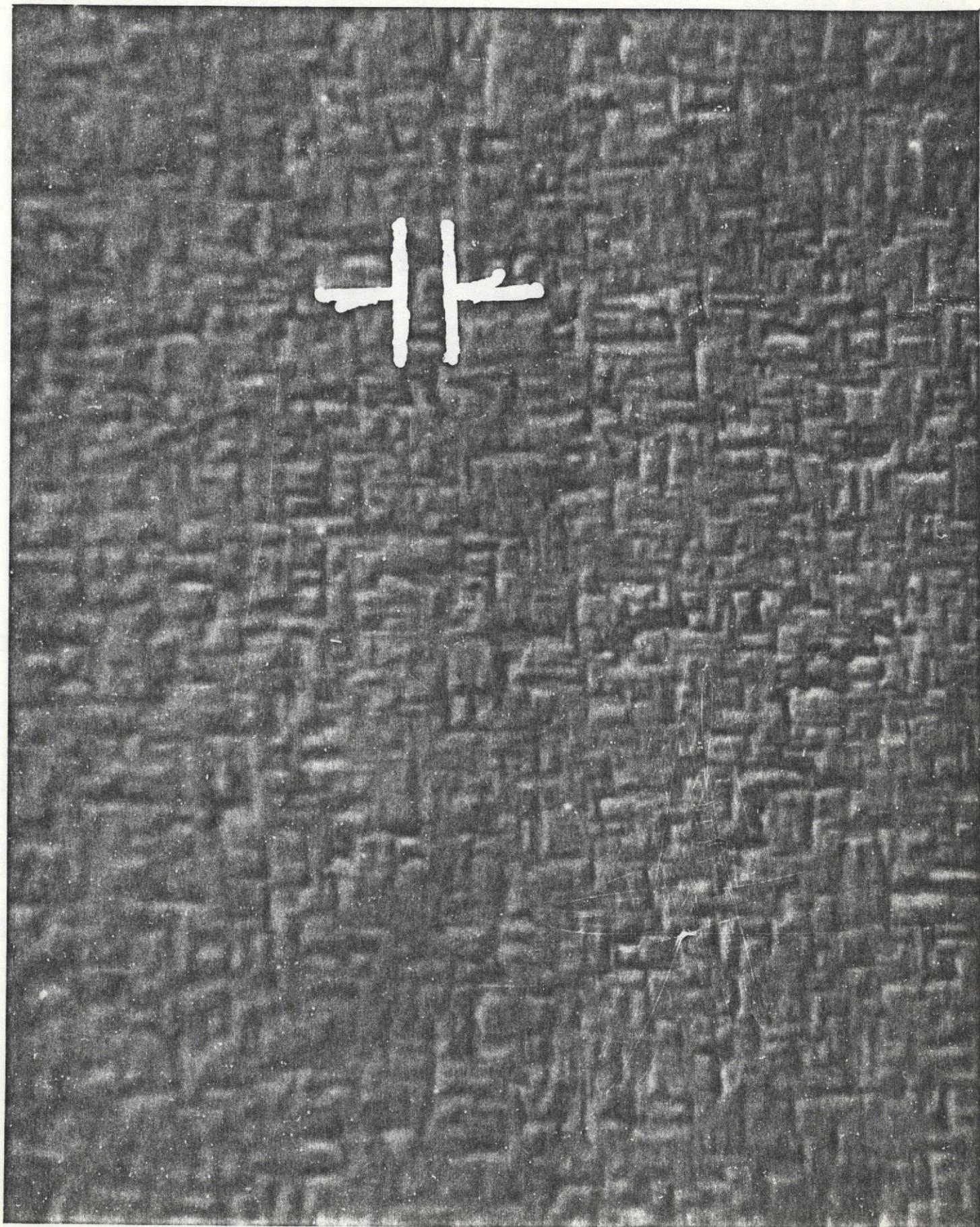


Figure 2b

Figure #3
Luminescence of ZnSe Layers
Grown from a Crushed-Crystal Source

The numbers in parentheses are the scaling factors used to multiply the intensity of the original data in preparing this figure. The relationship between run number and the accumulated hours of source use is #7-20 hrs., #10-39 hrs., #13-65 1/2 hrs., #17-107 hrs., #18-119 hrs., and #19-131 hrs. Run #17 employed a GaAs substrate.

Figure #4
Detail of Blue Luminescence of
ZnSe Layers

The spectra of the layer obtained from run #13 is typical of those obtained from runs #12 through #16. Run #18 was preceded by one run on a GaAs substrate. The numbers in parentheses are scaling factors for the data as defined in Figure 3.

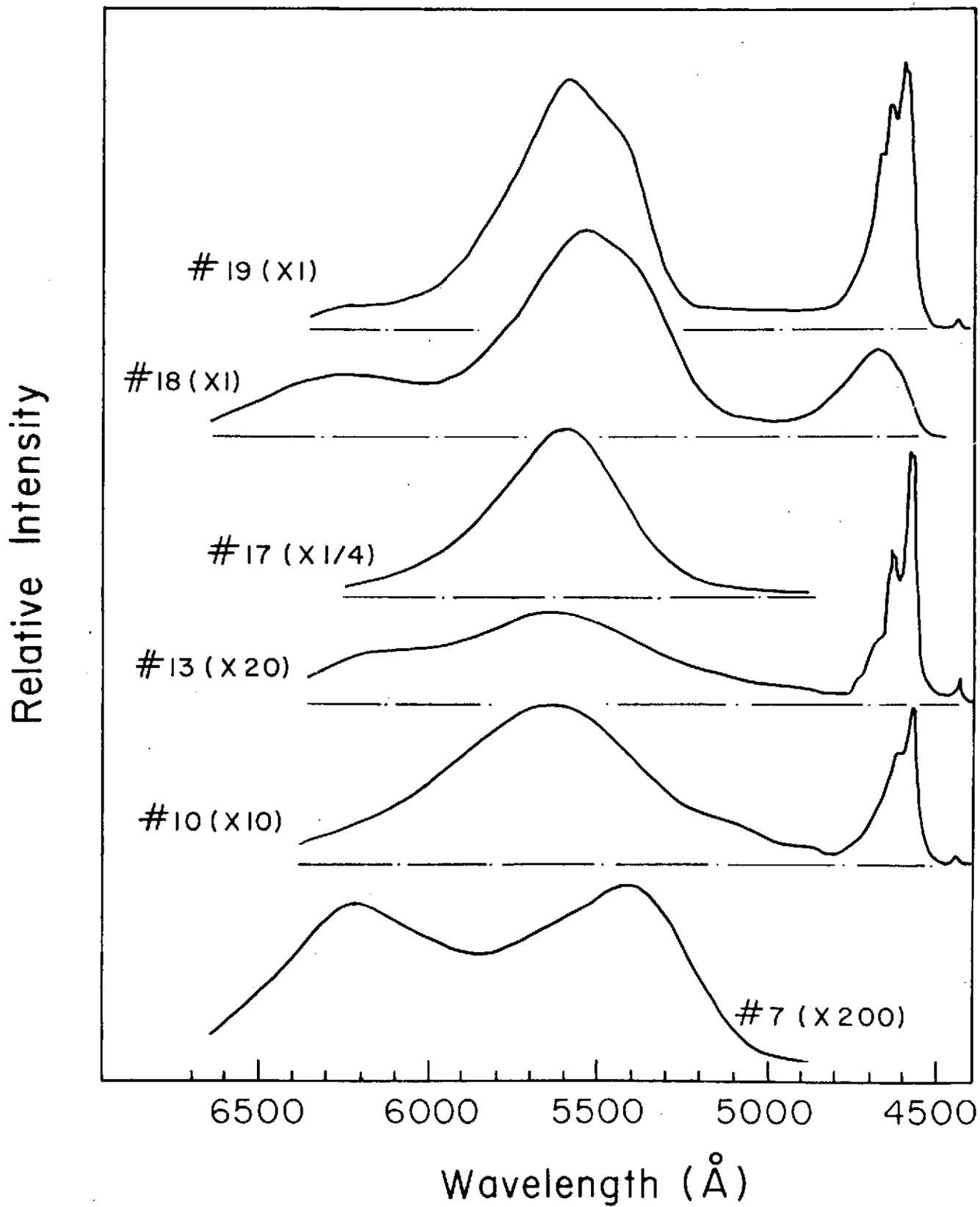


Figure 3

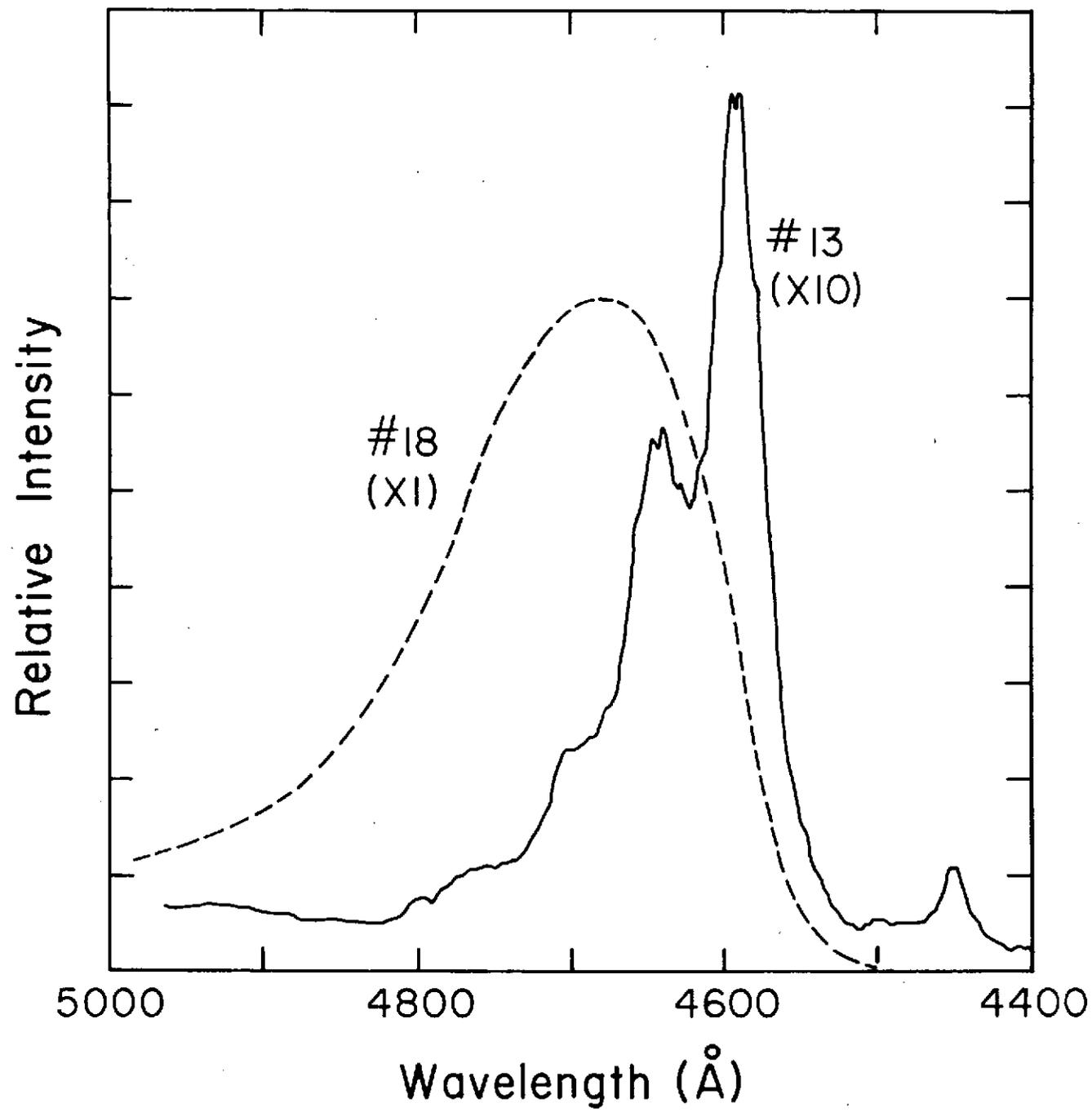


Figure 4